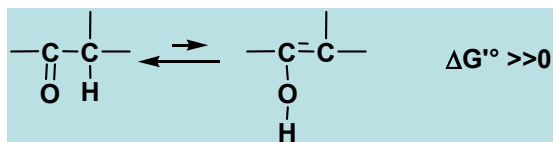


Ketoenolic tautomerism

Ketoenolic tautomerism



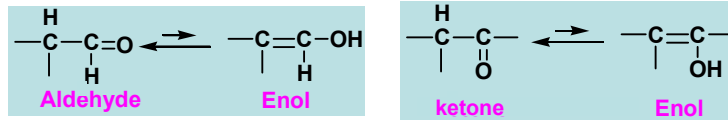
▪ Ketoenolic tautomerism is always endergonic when the enol is formed. Inversely, the return to aldehyde or ketone liberates energy.

▪ Therefore, Ketoenolic tautomerism is reactions coupled to themselves (double ketoenolic tautomerism) or to other reactions.

Double ketoenolic tautomerism are reactions that allow the transposition and isomerization of sugars. In the case of isomerization the reaction is reversible.

Ketoenolic tautomerism

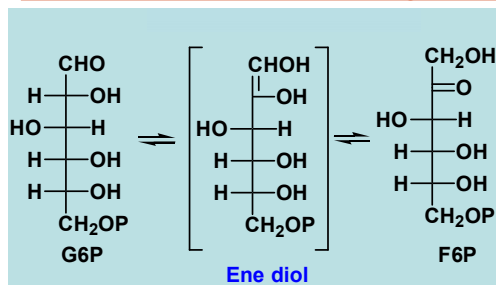
- Substrates: these reactions take place in substrates having a C-H in position α of an aldehyde or a ketone.



endergonic reactions ($\Delta G^{\circ} > 0$), so they are directed to left.

Ketoenolic tautomerism reactions are very quick, they occur in the enzyme active site catalyzing the associated coupled reaction.

Mechanism of transposition of sugars or P-sugars (ex ; G6P \rightleftharpoons F6P)



Fixation of G6P on the isomerase stabilize the enediol, this allows the transposition

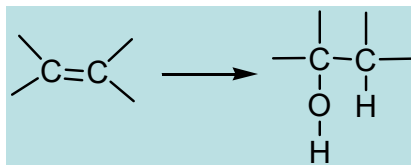
Hydration Dehydration

Hydration and dehydration reactions are all reversible ($\Delta G'^{\circ}=0$)

However, a polarizing effect is required and most often obtained by previously synthesizing **coenzyme A condensates**.

Hydration Dehydration

▪ Hydration involves the addition of a entire H_2O molecule into a double bond : in general carbon = carbon.



▪ The $C=C$ function must be at the vicinity of an electron attractor function. If the polarization is not sufficient, an activator coenzyme (most times $HSCoA$) is fixed into the vicinity of a $C-C$ that will then be transformed into the $C=C$ to be hydrated (see **Lynen catabolism**).

▪ Hydration and dehydration reactions are always reversible.

Conclusion : Types of reactions

Transformations of aliphatic compounds in the metabolic pathways always involve one or several of the simple reactions on one of the 5 categories:

(The transformation of aromatic compounds is more complex).

Major processes :

Oxidation / reduction

Hydrolysis / condensation

C-skeleton synthesis / C-skeleton breakdown

Minor processes:

Ketoenolic tautomerism

Hydration / dehydration

In the examination you will identify the reaction(s).

The sub-types (isomerization, decarboxylation...) will be considered only if the type of reaction is correctly mentioned.

For coupled reactions, you will have to mention all of them

(for ex. Oxidation + condensation)

Examples : Glycolysis and fatty acid catabolism (Lipid catabolism) involve the 5 types of reactions :

"Hydrolyse - Condensation " : action of a ligase and a thiolase (coupled reactions)

- **Hydrolysis** is exergonic and condensation is endergonic.
- **Condensation** is often coupled with a hydrolysis, while **C-C bond breakdown** is coupled with an oxidation.

"C-C bond breakdown " :

With few exceptions, C-C bond synthesis and breakdown are not red-ox : the reduction corresponding to C-C bond breakdown is compensated by an oxidation.

"Oxido-reduction" : action of dehydrogenases NAD⁺ or FAD dependent

- **FAD** allows oxidation of alkyl groups (function degrees=0). It requires an activated/mobile H in the vicinity of the reactive C-H.
- **NAD⁺** allows oxidation of functions with function degrees = or > 1.

"Hydration" : action of hydratase

- **Hydration - dehydration** reactions are reversible ($\Delta G^\circ=0$)

Ketoenolic tautomerism

- Ketoenolic tautomerism reactions are endergonic in the directions of enol formation ($\Delta G^\circ>0$).
- Thus, these reactions are always coupled to other reaction, many times the inverse ketoenolic tautomerism (sugar transposition by double Ketoenolic tautomerism) or others (degradation of PEP).